CHESTER LabNet

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Chester LabNet

Standard Operating Procedure
XR-006.01

Analysis of Elements in Air Particulates
by X-Ray Fluorescence (Kevex 771)

Approvals:

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REVIEW HISTORY

Review date:	Changes made:	Changes made by:
8/6/03	Minor text canges. Made corrections to title page and header.	Paul Duda
10/15/02	No changes. Date of origination. SOP based on XR-002 with changes in procedure for Kevex 771 software.	Paul Duda

ANNUAL REVIEW

The undersigned attests that this standard operating procedure has undergone annual review for adherence to current practices and the latest QA/QC protocols:

signature	printed name/title	date

Analysis of Elements in Air Particulates
by X-Ray Fluorescence (Kevex 771)

1.0 Scope and Application

1.1 This method is applicable to the quantitative analysis of aerosols deposited on a variety of filter types for the elements Na through U.

1.2 This method is applicable to the quantitative analysis of resuspended solids deposited on a variety of filter types for the elements Na through U, when first resuspended onto a variety of filter media following SOP XR-001.

2.0 Summary

2.1 Atoms in the sample are excited from their ground state to higher energy levels by X-radiation from an X-ray tube. These excited atoms emit discrete energy X-rays as they return to their normal ground state energy level. The energy of these emitted X-rays is characteristic of the excited element and is used to identify the element in the spectrum. A silicon-lithium crystal detector measures the change in the electronic field generated by the release of the eV charge during elemental excitation. This change in the field is proportional to the number of excited atoms, and is used to quantitate a specific elements concentration through a direct comparison with standards

3.0 Sampling and Storage

3.1 Samples may be stored as per client's requirement, but analysis is performed at room temperature, and in most cases under vacuum.

4.0 Apparatus

4.1 Instrument. Kevex Model Delta 771 energy dispersive XRF (EDXRF) equipped with a water-cooled end-window X-ray tube with a rhodium anode and a peak operating power of 60kV and 3.3 mA.

4.2 Accessories

    4.2.1   HDPE filter holders with retaining rings purchased from VHG Labs to hold 37mm (part # PFM-37) or 47mm (part # PFM-47) diameter filters at a fixed distance from the X-ray source. Each retaining ring has a unique identifier written on it.

    4.2.2   Gepe Model 4302 slide storage chest.

    4.2.3   Forceps.

    4.2.4   25mm filter holder adapters

    4.2.5   Kimwipes

4.3 Thin Film Calibration Standards

    4.3.1   Micromatter Inc. vapor deposit of single or two non-interfering elements onto thin mylar film.

    4.3.2   EPA organo-metallic acetate film, usually with two non-interfering elements.

    4.3.3   NIST SRM's 1832 and 1833 multi-element vapor deposits on glass films.

5.0 Reagents

5.1 95% ethanol

5.2 Liquid Nitrogen

6.0 Calibration/Preparation

    6.1 Sample loading

        6.1.1   Obtain an XRF Analysis Request Form (Figure 1.).

        6.1.2   Retrieve the samples indicated in the LIMS ID column of the request form.

        6.1.3   Prepare the work area: Filter loading is done in the laminar flow hood.

            6.1.3.1 Turn the hood blower and lights on

            6.1.3.2 Clean the work surface with a Kimwipe and ethanol

            6.1.3.3 Lay out a paper towel in the hood.

            6.1.3.4 Clean a pair of forceps and the filter loading block with Kimwipes and ethanol and place on the towel.

            6.1.3.5 Place the filters to be analyzed, the slide storage chest, the XRF request form and a pen in the hood.

        6.1.4   Load the filters:

            6.1.4.1 Clean all XRF sample holders with ethanol-soaked Kimwipes, being careful to not erase the filter holder IDs.

            6.1.4.2 Place appropriate sized filter holder on the filter loading block and then select the filter to be loaded.

            6.1.4.3 Remove the filter from its container and place deposit side down in the filter holder.

            6.1.4.4 Use forceps and handle the filter only around its perimeter. If the forceps touch the deposit, clean forceps before proceeding.

6.1.4.5 Ensure that deposit area is within the detection area (eg near the center of the filter).

6.1.4.6 Choose the appropriate retaining ring and snap it into place so that the filter is held in place without wrinkles or other misalignment. The retaining rings are labeled in batches with a letter/symbol and numbers (1-10). For example, the first set of rings is labeled A1, A2, A3…A10, the second set is labeled B1, B2, B3…B10, etc.

6.1.4.7 Note the condition of the filter and record any comments on the XRF request form that may apply to the XRF analysis, such as non-uniform deposit, wrinkled filter, etc. Filters with loose deposits should <u>not</u> be analyzed.

6.1.4.8 Place the numbered filter holder in the slot that the retaining ring was taken from. IT IS EXTREMELY IMPORTANT TO MATCH FILTER NUMBER TO LOCATION NUMBER ON XRF REQUEST FORM.

6.1.4.9 The filter container should be placed back in the tray it was originally stored in.

6.1.4.10 Continue steps 6.1.4.1 through 6.1.4.9 for the remaining filters (maximum of ten).

6.1.4.11 The quality assurance standard (QS) is permanently loaded and is not stored in the sample case.

6.1.4.12 Write the batch letter/character (A, B, etc.) in the upper left-hand corner of the XRF request form and initial and date the line labeled 'Load" on the upper-right-hand section of the XRF request form.

6.1.5 Queue samples:

6.1.5.1 Place the sample case in the queue awaiting XRF analysis.

6.1.5.2 Place the XRF request form(s) in the associated instrument specific queue.

6.1.5.3 Place the slide storage chest in the appropriate staging area (active sample refrigerator or on the counter in the XRF area)

6.1.5.4 Return the filter containers back to where they were originally stored.

6.2 Kevex Start Up - This is the procedure for starting the Kevex if the X-rays have been off for more that 12 hours.

6.2.1 With instrument off, <u>carefully</u> raise the chamber lid until the latch at the far left end of the chamber catches.

6.2.2 Initiate Spectrometer:

6.2.2.1 Turn the key ON. If the key already is ON, then turn it OFF and then back ON.

6.2.2.2 The sample tray should now be located at position 1, the X-ray tube should be in the secondary excitation position, and the secondary target should be zero.

6.2.3 <u>Carefully close the chamber lid on the Kevex</u>*. If the lid is suddenly dropped, the resulting pressure may be sufficient to rupture the thin Be windows on the X-ray tube and detector.*

6.2.4 Reinitialize electronics communications:

6.2.4.1 Cold reboot the PC. The following programs will automatically open: Kevex WinXRF, Kevex WinXRF Spectrum Display Panel, Kevex WinXRF Monitor.

6.2.4.2 In the Kevex WinXRF Monitor program chose 'File', then 'Download Front-End'. At this point you will be prompted. Chose 'OK'. If at this point a communication error message appears, press the 'reset' button on the bin

module next to the PC tower with the tip of a pen or pencil, and click 'OK'. After the front-end software has finished downloading, minimize the Kevex WinXRF Monitor window.

6.2.4.3 In the Kevex WinXRF Spectrum Display Panel window select 'Setup', then 'Connect', then "Activate'. At this point, the two arrows below the 'Print' option in the window should change color from red to black, and should now be parallel horizontally.

6.2.5 Begin x-ray tube warm up:

6.2.5.1 In the Kevex WinXRF Spectrum Display Panel window set the 'mA' to 0.1 and the 'kV' to 10, then press the white 'X-RAY ON' button at the front panel of the Kevex. This should cause the red 'X-RAY ON' light to come on at the front panel of the Kevex.

6.2.5.2 Press the white 'X-RAY ON' button at the front panel of the Kevex. This should cause the red 'X-RAY ON' light to come on at the front panel of the Kevex.

6.2.5.3 To prevent undue wear on the X-ray tube anode, slowly ramp up the xray tube as per page 2-6 of the Kevex 'X-RAY TUBE, HIGH VOLTAGE POWER SUPPLY AND HEAT EXCHANGER USER'S MANUAL'. (See Appendix A)

7.0 Procedure

7.1 Kevex Operating Procedure - the Kevex operating manual should be reviewed before operating the instrument. One should be familiar with the hazards of incorrect operation and the safety systems of the instrument.

7.2 Start Analysis Run

7.2.1   In the Kevex WinXRF Spectrum Display Panel window, set the 'mA' to '0.1' and the kV to '10'. Set 'atm' (atmosphere) to 'air'.

7.2.2   When conditions have stabilized, press the red 'X-rays Off' button on the front panel of the Kevex and carefully raise the chamber lid until the latch engages.

7.2.3   Remove the sample tray from the Kevex chamber.

7.2.4   Place the sample tray in the staging area and remove any samples that may be residing in the sample positions, returning the samples to their proper positions in the proper sample case. The quality assurance standard (QS) remains in the tray and always resides in position '1'.

7.2.5   Transfer each filter holder in sequence to a numbered position in the Kevex sample tray. Record the tray position to the left of the filter holder number on the run sheet. The Kevex tray has 16 positions, so that up to 15 samples may be analyzed along with the QS during each analysis run. When properly loaded, the deposit side of the filter should be facing down and the notch in the filter holder will be in the upper right hand corner of the sample tray opening.

7.2.6   Replace the sample tray in the Kevex chamber, being careful to orient the two holes in the tray to the correct posts on the sample-advance motor. Carefully lower the chamber lid.

7.2.7   If the analysis calls for vacuum, set 'atm' to 'vac' in the Kevex WinXRF Spectrum Display Panel window and make sure the lid is sealed by trying to lift it. If the lid is not sealed, check that the gasket is properly positioned and hold lid down until sealed.

7.2.8   Make sure that the current and voltage are set at 0.1 mA and 10 kV. Turn X-rays 'ON' at Kevex front panel.

7.2.9   Setup the XRF analysis run in the WinXRF program.

7.2.9.1 Using Windows Explorer, create a copy of file "01master.kvx" in the winxrf directory. "01master.kvx" is an empty template file.

7.2.9.2 Rename the file "Copy of 01master.kvx" to "CNNN-XXX.kvx" which corresponds to the run number listed on the XRF Analysis Request Form that is to be analyzed.

7.2.9.3 Close Windows Explorer

7.2.9.4 Associate the new .kvx file with unit 0 in WinXRF
   7.2.9.4.1   In the WinXRF program, click"file" and then "kvx library". Select the file created above and click "OK".
   7.2.9.4.2   Verify that the selected file is blank by clicking "file" and then "WinXRF File Manager". A new window will appear. Click on "spectrum". If everything was done properly, no files should appear.

7.2.9.5 Set up the job chain. The job chain for a routine analysis run will contain five jobs, **qs-print**, the sample analysis job (**p6t**), **qs**, the replicate analysis job (**p5t**) and **idle**.
   7.2.9.5.1   Click on "Jobs" on the WinXRF toolbar. This will open a new window titled "Job Manager".
   7.2.9.5.2   Select "qs-print.job".
   7.2.9.5.3   Click on "Samples" button.
   7.2.9.5.4   Click on the "Clear" button.
   7.2.9.5.5   Type the sample IDs in the corresponding spaces, with the QS standard always in the first position, the samples next and dummy IDs in any empty positions.
   7.2.9.5.6   On the sample wheel diagram, select only the QS standard.
   7.2.9.5.7   Click "OK". This will close the "Samples" window. Two windows will appear before closing the window, One saying "Save names file Traylist?" and another saying "Save Job File?". Click "Yes" for both questions.
   7.2.9.5.8   Add the job to the job chain by clicking the "ADD" button in the Job Manager window. The number of jobs in the job chain should go from 0 to 1.

7.2.9.5.9   Select the analysis protocol to be used for the samples, i.e. "p6t.job".

7.2.9.5.10   Click on the "Samples" button.

7.2.9.5.11   On the sample wheel diagram, select all the samples to be analyzed.

7.2.9.5.12   Click "OK". This will close the "Samples" window. Two windows will appear before closing the window, One saying "Save names file Traylist?" and another saying "Save Job File?". Click "Yes" for both questions.

7.2.9.5.13   Add the job to the job chain by clicking the "ADD" button in the Job Manager window. The number of jobs in the job chain should go from 1 to 2.

7.2.9.5.14   Select "qs.job" and add it to the job chain. The number of jobs in the job chain should go from 2 to 3.

7.2.9.5.15   To schedule the replicate, select the next lower protocol than the samples were originally analyzed by, i.e. if the samples were analyzed using "p6t.job", select "p5t.job".

7.2.9.5.16   Click on "Samples" button

7.2.9.5.17   Click on the "Deselect All" button below the sample wheel diagram and select the appropriate sample(s) to be reanalyzed as replicate(s).

7.2.9.5.18   Click "OK". This will close the "Samples" window. Two windows will appear before closing the window, One saying "Save names file Traylist?" and another saying "Save Job File?". Click "Yes" for both questions.

7.2.9.5.19   Add the job to the job chain. The number of jobs in the job chain should go from 3 to 4.

7.2.9.5.20   Select "idle.job" and add it to the job chain. The number of jobs in the job chain should go from 4 to 5.

7.2.9.6   Click the "Run" button. This action will start the automated run and will open a new window labeled "Kevex Job Report".

7.2.9.7   Drag the "Kevex Job Report" window to the lower righthand section of the screen so that you can see the livetime counter and the spectrum acquiring.

7.2.9.8   Click on the "Kevex WinXRF Spectrum Display Panel" window to make it active. If the "Kevex Job Report" window is the active window, it is possible to inadvertently abort the run when interrupting the screen saver.

7.2.10   On the XRF request form record your initials in the space labeled 'Primary:', the date and time in the space labeled 'Date Analysis Initiated:'.

7.2.11   In the Kevex Logbook enter the date, time, analyst's initials, run number, analysis protocol, and number of samples.

7.3 Completion of the run:

7.3.1   After the run has successfully completed, the spectral files will be located in the file created in step 7.2.9.2 in the WinXRF subdirectory on the hard drive. Using Windows Explorer, copy this file to the WinXRF directory of the R: drive (Rick2).

7.3.2   Move to the data processing computer (Rick2).

7.3.3   Convert kvx library spectrum files to text files that can be read by Excel processing file.

7.3.3.1   Open the WinXRF program.

7.3.3.2   In the WinXRF program, click"file" and then "kvx library". Select the file created step 7.2.9.2 and click "OK".

7.3.3.3   Type "run export". This program will prompt you through the conversion process. After answering all the questions, there should be .sp1 through .sp5 files for every sample analyzed in the run. These files will be used to process the data. (SOP XR-005)

7.3.4   At this point, process the QS data as described in SOP XR-005.

7.4 After ensuring that the QS sample has passed for this run, unload the XRF:

7.4.1   Remove the Kevex sample tray

7.4.2   Remove the samples from the sample tray and place back in the appropriate sample box. It is extremely important to match filter number to location number to XRF request form.

7.4.3   The samples are now ready to be transferred from the XRF sample holders back into their shipping containers and either archived or returned to the client.

7.5 At this point, the next scheduled XRF analysis may be initiated.

7.6   Instrument shut-down.

    7.6.1   When the XRF instrument is not in use, the X-rays are kept on at a low 'standby' power setting which acts to prolong the life of the X-ray tube.

    7.6.2   Set the tube power to 10 kV and 0.1 mA.

    7.6.3   Set the tube to the secondary target position

    7.6.4   Set the target wheel to position zero.

8.0 QA/QC

8.1 Quality Assurance Standard (QS). The QS is a multi-element thin film vapor-deposited standard on mylar manufactured by Micromatter Inc. The QS measurements are considered to be a reliable approximation of the precision of the instrument between the time of analysis and the time of calibration.

    8.1.1   Frequency: once, at the end of each analytical run

    8.1.2   QC statistic: percent recovery

    8.1.3   Control limits: 90-110 %

    8.1.4   Corrective action: terminate analysis, determine cause of QS failure. Failure necessitates re-analysis of any excitation condition(s) falling outside the limit. Repeated failure requires a recalibration of any excitation condition(s) not meeting the required limits and reanalysis of the samples associated with the failed QS. See analyst's note 11.1 for possible sources of QS failures.

    8.1.5   Note: See section 9 for a description of the QS true value determinations.

8.2 Laboratory Replicate.   This is a sample which is analyzed twice.

    8.2.1   Frequency: once per analytical batch of ten client samples.

    8.2.2   QC Statistic: relative percent difference (RPD) of both the sample results and the uncertainties of the sample results (δ_{RPU}) for all results greater than three times the uncertainty of that analyte.

    8.2.3   Control limits: Average analyte score for the sample must exceed 1.5. See section 9.2 for the calculations relating to scoring of samples.

    8.2.4   Corrective action: re-analyze a different sample and replicate. If control limits are still exceeded, troubleshoot the instrument and reanalyze all samples associated with that replicate.

    8.2.5   Note: The replicate is usually run at the next lowest protocol so that the detection limits are approximately 1.414x higher than the original analysis.

8.3 NIST weekly accuracy check (NIST check). These standards are thin film standard prepared and certified by NIST. The frequency of this analysis is limited by the fragile nature of the standards. Elements analyzed are Al, Si, K, Ca, Ti, V, Mn, Fe, Cu, Zn, and Pb. Each element is analyzed in each pertinent excitation condition.

    8.3.1   Frequency: once per week

    8.3.2   QC statistic: analytical result

    8.3.3   Control limits: within the NIST certified uncertainty for each analyte

    8.3.4   Corrective action: terminate analysis, recalibrate the excitation condition in which the failure occurs.

9.0 Calculations

9.1 Calculation of QS standard percent recovery:

The QS multielement thin film standard is analyzed several times during calibration, and the gross counts for elements Si, Ti, Fe, Se, and Cd in their Kα windows, and Pb in its Lβ window are averaged. These averaged values are entered into the QS data processing program. The QS is then run concurrent with each analytical run of samples and the gross counts for each element in each excitation condition are compared with those obtained during calibration.

Percent recoveries are calculated as follows:

$$R_{i,j} = U_{i,j} / C_{i,j} * 100$$

where: $R_{i,j}$ = recovery for element i in excitation condition j.
$U_{i,j}$ = gross counts per second for element i in excitation condition j obtained during analysis of samples.
$C_{i,j}$ = the averaged gross counts per second for element i in excitation condition j from the calibration runs.

9.2 Scoring of Replicate Samples:

For a given sample, all analyte results which exceed three times the uncertainty for that analyte is given both a score and a qualifier. The score is a numerical value assigned to a qualifier to aid in determining the overall score of the replicate sample. The qualifier and score is determined by comparing the relative percent difference of the analyte result to the relative percent *uncertainty* of the analyte result.

9.2.1   The relative percent difference (RPD) of the analyte result is calculated as follows:

$$RPD = [(X_1 - X_2) / ((X_1 + X_2) / 2)] \times 100$$

where: X_1 = original sample concentration

X_2 = replicate sample concentration

9.2.2   The relative percent uncertainty (RPU) of the uncertainties is calculated as follows:

$$\delta_{RPU} = [((\delta_o^2 + \delta_r^2)^{1/2}) / ((X1 + X2) / 2)] \times 100$$

where: δ_{RPU} = the relative percent uncertainty of each analyte

δ_o = the uncertainty for a particular analyte for the original analysis

δ_r = the uncertainty for a particular analyte for the replicate analysis

X1 = the original sample concentration

X2 = the replicate sample concentration

9.2.3   Each replicate analyte is graded and qualified as follows:

Condition	Score	Qualifier
$RPD \leq \delta_{RPU}$	+2	+
$\delta_{RPU} < RPD \leq 2 \times \delta_{RPU}$	+1	0
$2 \times \delta_{RPU} < RPD \leq 3 \times \delta_{RPU}$	-1	-
$RPD > 3 \times \delta_{RPU}$	-2	-

9.2.4   The overall score of the replicate is calculated as follows:

$$S_f = \frac{\sum S_i}{n}$$

where: S_f = the final grade

S_i = each individual analyte score ('+2', '+1', '-1', or '-2')

n = the total number of analytes whose original concentration

exceeds 3x its uncertainty

10.0 References

10.1 Kevex Operator's Manual

10.2 Practical X-Ray Spectrometry, R. Jenkins and J.L. De Vries, second edition, Philips
Technical Library, Springer-Verlag New York Inc.

10.3 X-Ray Fluorescence Analysis of Environmental Samples, Jaklevic, et al, Ed. by T.G. Dzubay,
Ann Arbor Sci.

10.4 Self Absorption Corrections for X-Ray Fluorescence Analysis of Aerosols, T.G. Dzubay and
R.O. Nelson, in Advances in X-Ray Analysis, Vol 18, 619-631.

10.5 Quantitative Analysis of Aluminum and Silicon in Air Particulate Deposits on Teflon
Membrane Filters by X-Ray Fluorescence Analysis, J.A. Cooper, L.M. Valdovinos, J.R.
Sherman, W.L. Pollard, R.H. Sarver, and J.K. Weider, report by NEA, Inc., Beaverton, OR,

July 15, 1987.

10.6 Round Robin Evaluation: Elemental Analysis of Bulk Samples and PM_{10} Loaded Teflon Filters, presented at the 82nd Annual Meeting of AWMA, Anaheim, CA, June 24-30, 1989.

11.0 Analyst Notes

11.1 QS and NIST failures indicative of XRF system malfunctions may include:

11.1.1 Processing of sample through incorrect spreadsheet. Prior to any other troubleshooting, analyst should verify that the QS or NIST standard was processed through the appropriate spreadsheet (eg a Teflon QS will fail if processed through the quartz QS spreadsheet).

11.1.2 Vacuum failure/decay where the lower energy elements Si and Ti are readily absorbed by the Ar in the atmosphere. Si will exhibit the lowest recovery, then Ti < Fe < Se < Pb < Cd.

11.1.3 Channel drifting will cause peaks to shift so that recoveries are low for all elements. Check the QS spectra for shifting and correct by recalibrating the channels (see SOP XR-004).

11.1.4 Degradation in peak intensity in all excitation conditions can signal a decline in X-ray tube performance.

11.1.5 Loss of resolution (peak broadening) is a sign of detector degradation, and may indicate a low liquid nitrogen level, or loss of vacuum behind the Be window.

XRF Analysis Request Form

Date of Request: _____   Initial:

Date Results Required: _____   Load:_____

Client Name: _____

Run Number: _____   Primary:_____

Protocol: _____

Sample Description: _____   Secondary:_____

Total # of Samples: _____

Report Number: _____   QA:_____

Date Analysis Initiated: _____

Date Data Processed: _____   Unload:_____

Date Worklist Released: _____

Comments: _____

Cond	LT	Target	Prefilter	Voltage	Current	Disk #
0						
1						
2						
3						
4						
5						

Pos.	LIMS ID	S	Blank	Deposit Area	Mass	Comments
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16	*QS*					

Figure 1. XRF Run Sheet

Kevex 771 QS Report

02-QS044B

Condition 1

Livetime	Target	Filter	kV	mA
100	Direct	Cellulose	6	0.50

	Gross Counts	Normalized	Gross Counts per Second		Average Cts/Sec	Recovery	

	Gross Counts	Normalized Gross Counts per Second		Average Cts/Sec	Recovery	
Si	108934	2178.68		2277.09	0.957	PASS

Condition 2

Livetime	Target	Filter	kV	mA
100	FE	-	35	1.00

	Gross Counts	Normalized Gross Counts per Second		Average Cts/Sec	Recovery	
Ti	31540	315.40		320.04	0.986	PASS

Condition 3

Livetime	Target	Filter	kV	mA
100	GE	-	45	1.00

	Gross Counts	Normalized Gross Counts per Second		Average Cts/Sec	Recovery	
Ti	19570	195.70		201.90	0.969	PASS
Fe	67850	678.50		665.41	1.020	PASS

Condition 4

Livetime	Target	Filter	kV	mA
100	Direct	Rh	35	1.00

	Gross Counts	Normalized Gross Counts per Second		Average Cts/Sec	Recovery	
Ti	1146	11.46		12.08	0.949	PASS
Fe	4168	41.68		42.95	0.970	PASS
Se	5283	52.83		52.09	1.014	PASS
Pb	6695	66.95		67.19	0.996	PASS

Condition 5

Livetime	Target	Filter	kV	mA
100	Direct	W	55	1.00

	Gross Counts	Normalized Gross Counts per Second		Average Cts/Sec	Recovery	
Cd	11753	117.53		118.99	0.988	PASS

Figure 2. Example QS results page

REPLICATE REPORT

Original ID: 02-T5786
Replicate ID: RT5786

Deposit Mass: 214   μg
Deposit Area: 11.3   cm²
Particle Size: F

Element	Original ug/cm2			Replicate ug/cm2			Differenc ug/cm2				RPI		
Na	0.0921	+-	0.0452	0.0381	+-	0.0476	0.0540	+-	0.0656				
Mg	0.0000	+-	0.0158	0.0325	+-	0.0176	-0.0325	+-	0.0236				
Al	0.0271	+-	0.0077	0.0173	+-	0.0083	0.0098	+-	0.0114	+	44.0	+-	51.2
Si	0.0965	+-	0.0116	0.0957	+-	0.0118	0.0007	+-	0.0165	+	0.8	+-	17.2
P	0.0000	+-	0.0026	0.0000	+-	0.0030	0.0000	+-	0.0040				
S	0.5519	+-	0.0623	0.5804	+-	0.0658	-0.0285	+-	0.0906	+	-5.0	+-	16.0
Cl	0.0104	+-	0.0038	0.0124	+-	0.0046	-0.0019	+-	0.0059				
K	0.0527	+-	0.0062	0.0589	+-	0.0071	-0.0061	+-	0.0094	+	-11.0	+-	16.8
Ca	0.0437	+-	0.0052	0.0446	+-	0.0055	-0.0009	+-	0.0076	+	-2.1	+-	17.2
Sc	0.0000	+-	0.0010	0.0006	+-	0.0013	-0.0006	+-	0.0017				
Ti	0.0089	+-	0.0011	0.0109	+-	0.0015	-0.0020	+-	0.0019	0	-20.6	+-	18.8
V	0.0011	+-	0.0006	0.0002	+-	0.0009	0.0009	+-	0.0011				
Cr	0.0006	+-	0.0006	0.0013	+-	0.0008	-0.0007	+-	0.0010				
Mn	0.0004	+-	0.0009	0.0040	+-	0.0012	-0.0036	+-	0.0015				
Fe	0.1003	+-	0.0053	0.1014	+-	0.0056	-0.0011	+-	0.0076	+	-1.1	+-	7.6
Co	0.0000	+-	0.0008	0.0000	+-	0.0010	0.0000	+-	0.0013				
Ni	0.0000	+-	0.0005	0.0001	+-	0.0007	-0.0001	+-	0.0008				
Cu	0.0899	+-	0.0046	0.0902	+-	0.0048	-0.0003	+-	0.0067	+	-0.3	+-	7.4
Zn	0.0023	+-	0.0007	0.0033	+-	0.0010	-0.0010	+-	0.0012	+	-37.3	+-	43.9
Ga	0.0000	+-	0.0015	0.0000	+-	0.0022	0.0000	+-	0.0026				
As	0.0028	+-	0.0010	0.0001	+-	0.0013	0.0027	+-	0.0017				
Se	0.0013	+-	0.0008	0.0005	+-	0.0012	0.0007	+-	0.0015				
Br	0.0044	+-	0.0009	0.0034	+-	0.0012	0.0010	+-	0.0015	+	25.1	+-	38.4
Rb	0.0000	+-	0.0009	0.0000	+-	0.0012	0.0000	+-	0.0015				
Sr	0.0000	+-	0.0010	0.0001	+-	0.0014	-0.0001	+-	0.0018				
Y	0.0015	+-	0.0012	0.0000	+-	0.0017	0.0015	+-	0.0021				
Zr	0.0029	+-	0.0015	0.0000	+-	0.0020	0.0029	+-	0.0025				
Nb	0.0005	+-	0.0017	0.0000	+-	0.0023	0.0005	+-	0.0029				
Mo	0.0028	+-	0.0019	0.0000	+-	0.0027	0.0028	+-	0.0033				
Ag	0.0000	+-	0.0037	0.0042	+-	0.0055	-0.0042	+-	0.0066				
Cd	0.0017	+-	0.0039	0.0000	+-	0.0054	0.0017	+-	0.0066				
In	0.0000	+-	0.0041	0.0000	+-	0.0055	0.0000	+-	0.0068				
Sn	0.0192	+-	0.0070	0.0148	+-	0.0068	0.0044	+-	0.0097				
Sb	0.0021	+-	0.0055	0.0058	+-	0.0074	-0.0037	+-	0.0092				
Cs	0.0091	+-	0.0144	0.0174	+-	0.0199	-0.0083	+-	0.0245				
Ba	0.0189	+-	0.0196	0.0466	+-	0.0275	-0.0277	+-	0.0338				
La	0.0000	+-	0.0265	0.0000	+-	0.0368	0.0000	+-	0.0453				
Ce	0.0071	+-	0.0373	0.1106	+-	0.0529	-0.1035	+-	0.0647				
Hg	0.0000	+-	0.0017	0.0000	+-	0.0023	0.0000	+-	0.0029				
Pb	0.0005	+-	0.0022	0.0006	+-	0.0030	-0.0001	+-	0.0038				

RPD: Relative Percent Difference (X1-X2)/[(X1+X2)/2]*100. RPD is calculated when original value is greater than

Figure 3. Replicate sample report.

Chester LabNet - Portland

XRF-771   ## XRF Analytical Quality Assurance Report

Client: Weekly NIST Check
Analysis Period: through April 3, 2002

1. Precision Data

Micromatter Multi-elemental Quality Control Standard: QS285

QC Standard Results

Analyte	n	Counts per Second			c.v.	%E
		Calib.	Meas.	S.D.		
Si(1)	2	1809.27	1790.16	83.61	4.67	-1.06
Ti(2)	2	296.08	285.67	20.49	7.17	-3.52
Fe(3)	2	629.65	625.45	2.33	0.37	-1.32
Se(4)	2	50.84	50.17	0.48	0.96	-1.32
Pb(4)	2	66.2	65.07	1.62	2.49	-1.71
Cd(5)	2	113.88	111.70	5.02	4.49	-1.91

2. Accuracy Data

NIST Standard Reference Materials: SRM 1832, SRM 1833

Analyte/ SRM	n	Certified Value(μg/cm²)	Measured Value (μg/cm²)					% Rec.
			High	Low	Average			
Al 1832	45	14.6 +/- .97	15.90	13.86	14.44	+/-	0.46	98.9
Si 1832	45	34.0 +/- 1.1	38.01	33.37	34.59	+/-	1.04	101.7
Si 1833	45	33.0 +/- 2.1	33.16	30.67	32.25	+/-	0.49	97.7
S 2708	45	2.46 +/- .25	2.57	2.28	2.44	+/-	0.08	99.0
K 1833	45	17.3 +/- 1.64	17.44	16.09	16.91	+/-	0.34	97.7
Ca 1832	45	19.4 +/- 1.30	21.35	19.95	20.74	+/-	0.34	106.9
Ti 1833	45	12.8 +/- 1.79	12.85	11.72	12.28	+/-	0.37	95.9
V 1832	45	4.70 +/- .49	4.95	4.37	4.64	+/-	0.17	98.6
Mn 1832	45	4.54 +/- .49	4.84	4.56	4.69	+/-	0.06	103.3
Fe 1833	45	14.2 +/- .45	14.49	13.97	14.21	+/-	0.13	100.1
Cu 1832	45	2.43 +/- .16	2.49	2.31	2.43	+/-	0.04	99.8
Zn 1833	45	4.01 +/- .23	4.07	3.82	3.95	+/-	0.05	98.4
Pb 1833	45	16.7 +/- .85	18.26	15.97	16.94	+/-	0.46	101.5

NIST: National Institute of Standards and Technology
% Rec: Percent Recovery = (Experimental/Given) x 100
n: Number of Observations
S.D.:   Standard Deviation
c.v.:   Coefficient of Variation = (S.D./Measured) x 100
% E: Percent Error = [(Measured-Calibrated)/Calibrated] x 100

Figure 4. Weekly NIST accuracy standard report.

Appendix A:

Stepwise warm up data for xray tube

Step	KV/mA	Time (min)
1	10 / 0.2	1
2	20 / 0.2	1
3	30 / 0.6	1
4	40 / 1.3	2
5	45 / 1.6	2
6	50 / 2.0	2
7	50 / 2.5	2
(8)	Add 2 kV each 30 seconds	